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14. ABSTRACT This program investigated the microstructure-properties relationship in the newly discovered high performance electroactive polymers: high energy irradiated P(VDF-TrFE) copolymers and P(VDF-TrFE) based terpolymers. The uniqueness of this class of new electroactive polymer is: (i) a high electric field induced strain with very little hysteresis; (ii) the material also exhibits a very high elastic energy density (1 J/cm ³); (iii) the high frequency capability of the strain response (100 kHz). Although many electroactive materials have been reported, this class of material is still the only one which can be applied to practical devices. The understanding of the fundamentals responsible for the large electromechanical responses in this class of polymers will provide interesting science on how defect structures affect the ferro-electric properties in polymers. Such an understanding will also lead to new directions to better control the material properties.					
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I. Abstract:

This program investigated the microstructure-properties relationship in the newly discovered high performance electroactive polymers: high energy irradiated P(VDF-TrFE) copolymers and P(VDF-TrFE) based terpolymers. The uniqueness of this class of new electroactive polymers is: (i) a high electric field induced strain with very little hysteresis; (ii) the material also exhibits a very high elastic energy density ($\sim 1 \text{ J/cm}^3$); (iii) the high frequency capability of the strain response ($> 100 \text{ kHz}$). Although many electroactive materials have been reported, this class of material is still the only one which can be applied to practical devices. The understanding of the fundamentals responsible for the large electromechanical responses in this class of polymers will provide interesting science on how defect structures affect the ferroelectric properties in polymers. Such an understanding will also lead to new directions to better control the material properties.

In addition, in this program we also investigate new approaches to significantly improve the dielectric properties of polymers so that the new electroactive polymers can be operated with low applied field and voltage.

II. Technology Section:

(2.1) Structure-property relationship in high energy electron irradiated copolymers

The micro-structural changes in high-energy electron-irradiated poly(vinylidene fluoride-trifluoroethylene) 68/32 mol% copolymer have been studied by x-ray diffraction, FTIR spectroscopy, and differential scanning calorimetry. The macroscopic polarization response in these materials was investigated by examining the dielectric and polarization behavior in a broad temperature and frequency range. It was found that besides reducing crystallinity in the copolymer film, irradiation produces significant changes in the ferroelectric-to-paraelectric phase transition behavior. The irradiation leads to a reduction in the polar domain size to below a critical size (\sim a few nm), resulting in the instability of the macroscopic ferroelectric state and transforming the structure of the crystalline region in the copolymer from a polar all-trans ferroelectric to a non-polar state represented by a trans-gauche conformation. However, a re-entrant polarization hysteresis was observed in the copolymers irradiated with higher doses ($> 75 \text{ Mrad}$). Therefore, there is an optimized dose that generates a copolymer with a nonpolar structure but relatively high crystallinity whose electromechanical performance is the best. In the copolymers in this optimum dose range, FT-IR data revealed that there is not much change in the molecular conformation with temperature, even as the temperature passes through the dielectric peak, indicating that there is no symmetry breaking in both the macro-scale and local level. Although the lattice spacing of the crystalline region along the molecular chain direction discontinuously changes between two special cases, the inter-chain spacing continuously changes with the irradiation dose, reflecting a strong intra-chain coupling between the non-polar and polar regions. On the other hand, the X-ray data reveal that the crystalline size perpendicular to the polymer chain does not change with irradiation until at doses exceeding 85 Mrad .

(2.2.1) Introduction

High-energy irradiation has been practiced widely to modify the properties of polymeric materials.^{1,2} The effect of high energy irradiation on the piezoelectric properties, crystal structures and polymer morphology of poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) copolymers has been investigated quite extensively.² For instance, Lovinger observed the polymorphic transformation in P(VDF-TrFE) copolymers under high-energy electron irradiation, where the ferroelectric β -phase is converted to a paraelectric-like structure.³ In addition, he found that the dosage required for this transformation increases with the VDF content in the copolymer, which was interpreted as arising from the increased close packing between the polymer chains in the copolymers with increased VDF content. In addition to the polymorphic transformation, irradiation also causes the conversion from the crystalline to amorphous phase due to crosslinking. At very high doses, the copolymer becomes totally amorphous. Macchi *et al.* also observed the disappearance of the ferroelectric phase in the copolymer due to irradiation, and the transformation of the dielectric behavior from a strong first order Ferroelectric-Paraelectric (F-P) transition peak to a broad dielectric peak at ambient temperatures much below the original F-P transition temperature in unirradiated copolymers.^{4,5} The observed broad dielectric behavior in the irradiated copolymers was suggested to be an indication of a ferroelectric spin glass state.⁶

More recently, we reported that P(VDF-TrFE) copolymers with VDF contents below 70 mol% exhibit a slim polarization hysteresis loop at room temperature, following high-energy electron irradiation. Furthermore, due to the large magnitudes of conformational motions accompanying the interconversion between the all-trans (polar-phase) and trans-gauche (non-polar phase) states, the electric-field induced reversible polarization change results in a very high electrostrictive strain (~5%, Fig. 1(a)) and a high strain energy density, as well as a much improved electromechanical efficiency.^{7,9}

In addition, in a detailed study of dielectric and polarization behavior, it was shown that the irradiated copolymer exhibits a Vogel-Fulcher type dielectric relaxation as shown in Fig. 1(b),

$$f = f_0 \exp\left[\frac{-T_0}{T_m(f) - T_f}\right]$$

where f is the measuring frequency, $T_m(f)$ is the corresponding dielectric peak temperature, T_0 and f_0 are constants, and T_f is often regarded as the freezing temperature of a dipolar system (if the system is a dipolar glass). At temperatures below T_f , a ferroelectric state can be induced by a high electric field, while the remanent polarization increases gradually as the temperature is lowered. These features are very similar to those observed in inorganic relaxor ferroelectrics, and hence, the irradiated copolymer can be regarded as a polymeric relaxor ferroelectric, a "polar glass" system.^{7,10,11}

In this paper, we will discuss in detail the microstructural changes occurring in this class of materials and the effects of irradiation-induced defects on the polar domains and crystallite sizes. As reported recently, the copolymer with a VDF/TrFE ratio of 68/32 mol% exhibits the best electromechanical performance at room temperature after irradiation.^{8,9} Thus, we devote the current paper to a discussion of the macroscopic polarization responses and thermodynamic behavior of this composition in light of our analysis of its polarization, dielectric properties, and DSC data. It must be pointed out that although the macroscopic properties of the irradiated 68/32 copolymer were

observed to exhibit similar trends to those of the 50/50 copolymer studied earlier, a detailed study the 68/32 mol% composition was considered desirable to compare the material and microstructural properties of these two compositions and to provide a conceptually improved picture of relaxor behavior in polymers.

With regard to the structural characterization, in an x-ray diffraction study to be described in this paper, a (110, 200) peak was observed at room temperature and at a temperature exceeding the Curie temperature (previously in the irradiated 50/50 copolymer this peak was recorded only at room temperature¹³). These data lead to (1) a clearer picture of the micro-changes in crystalline sizes and lattice spacings perpendicular to the chain direction; and to (2) an improved understanding of the effects of irradiation-induced defects. More importantly, analysis of an x-ray diffraction (001) peak in the present study was analyzed to delineate the irradiation effect on the crystal size along the molecular chain direction and on the molecular conformations. The conformational changes were further confirmed by means of a Fourier transform infrared spectroscopic (FT-IR) study. When the results of the structural analysis are considered along with the macroscopic properties, a more refined picture emerges that describes the nature and role of the irradiation-induced defects.

(2.2.2) Experimental

P(VDF-TrFE) copolymer at the composition 68/32 mol% was chosen for this investigation. Among all the compositions investigated, this composition exhibits the highest room temperature electrostrictive responses. This is a result of the competition between the strain achievable in the copolymer due to conformational changes, which become large with VDF content, and the electron dose required to convert the copolymer into an electrostrictive material, which also increases with VDF content.¹² Increased electron dose will cause a large reduction in the crystallinity and as well as an increase in crosslinking density. These structural changes are detrimental to the electrostrictive strain.

The copolymer films used in this investigation were fabricated by solution casting and then uniaxially stretched at room temperature to 5 times of the original length. The thickness of films was in the range between 15 to 30 μm . The films were annealed before irradiation to improve the crystallinity. The irradiation was carried out in a nitrogen atmosphere at 100 °C with an electron energy of 1.2 MeV. It was found that irradiation at a temperature higher than the F-P transition reduces the doses needed to eliminate the room temperature polarization hysteresis and to achieve high electrostrictive strain. This could be due to increased chain mobility in the paraelectric phase, facilitating the polymorphic transformations. The irradiation was carried out in a dose range from 0 to 1.75×10^6 Gy. In order to stay consistent with our previous publications, the unit of dose used here is rad and Mrad (1 Mrad = 10^6 rad and 1 Gy = 100 rads).

The X-ray experiments were performed at the National Synchrotron Light Source beam line X18A of the Brookhaven National Laboratory (the X-ray wavelength was 1.2399 Å). The (200, 110) peak reported here was obtained using the reflection scan, while the (001) peak was obtained using the transmission scan. The FT-IR spectra at room temperature were obtained using a BIO-RAD WIN Fourier-transform IR spectrophotometer in the spectral region 4000–400 cm^{-1} . The high temperature FT-IR spectra were measured using a high temperature optical cell. The DSC data were taken

with a scan rate of 10 °C/min or 20 °C/min using (TA Instruments, DSC2920). Gold sputtered electrodes were used on films used for the characterization of the polarization responses. The dielectric properties as a function of the temperature of the films were measured with a LCR meter (HP 4284A) equipped with a temperature chamber with the scan rate of 2 °C/min. The polarization hysteresis loops were acquired by a computer controlled automatic system based on the Sawyer-Tower circuit.

(2.2.3) Results and Discussion:

(2.2.3.1) Polarization responses and transitional behavior in copolymers with different doses

The polarization hysteresis loops measured at room temperature at 1 Hz for the copolymer films treated with different doses are presented in Fig. 2(a). The maximum induced polarization under 150 MV/m field, P_s , the remanent polarization P_r , and coercive field E_c extracted from the polarization loops are summarized in Fig. 2(b). The data show a slow and continuous decrease of P_s with irradiation dose, a trend related to the conversion of the normal ferroelectric state into a non-polar state and the reduction of the crystallinity in the polymer, as has been discussed in an earlier publication.⁸ In contrast, a large drop in both E_c and P_r with dose is prominent, especially in the dose range between 35 Mrads and 70 Mrads. As a result, the sample irradiated with 75 Mrads exhibits the highest electrostrictive strain yet it displays only minor hysteresis. Interestingly, beyond 75 Mrads, there is an increased polarization hysteresis (re-entrant hysteresis). In some of the samples irradiated with 100 Mrads dose, this re-entrant hysteresis can be quite large as illustrated in Fig. 2(c). One possible cause for the observed re-entrant hysteresis (ferroelectricity) is the high crosslinking density in the polymer irradiated with high doses.¹³⁻¹⁵ Two crosslinking points located in close positions along the chains force a closer packing of the polymer chains in between, favoring the all-trans conformation and formation of small polar pockets. This re-entrant behavior is also observed in X-ray data presented below.

The evolution of the dielectric behavior with irradiation dose is shown in Fig. 3, which exhibits trends similar to those observed in Fig. 2. For instance, the peak temperature associated with the original F-P transition decreases with dose, indicating the weakening of the F-P transition; above 75 Mrads, it moves up slightly. For doses below 35 Mrads, the transition peak is still relatively sharp and exhibits thermal hysteresis. That is, the peak position measured during a heating scan is different from that during a cooling scan, an indication of a first order transition. For samples irradiated with doses above 35 Mrads, the dielectric peak broadens and thermal hysteresis disappears. As will be shown from the FT-IR data, in samples irradiated with doses near 70 Mrads, the broad dielectric peak actually does not correspond to a phase transition but the polymer remains in a non-polar phase even at temperatures far below the dielectric peak, reminiscent of the relaxor ferroelectric behavior in ceramics.

Interestingly, using the dielectric data, we found that the Vogel-Fulcher law can, in fact, be used to fit the change of the dielectric peak temperature with frequency, even for the unirradiated copolymer, which is a typical normal ferroelectric. This observation supports an early theoretical result by Tagantsev that the Vogel-Fulcher dielectric behavior can also be observed in a dielectric system with a broad dielectric relaxation distribution that broadens gradually with decreasing temperature.¹⁶ The gradual freezing

of a dipolar system with temperature is not a necessary condition for the presence of Vogel-Fulcher dielectric behavior.

DSC data for the irradiated copolymers are summarized in Fig. 4 (acquired during heating of the samples). The data show that in general both the peak temperature and the enthalpy of the melt decrease with dose, due to the decrease in crystallinity and reduced crystalline ordering in the polymer, except for the samples irradiated at 10 Mrads. The melt enthalpy of the copolymer irradiated with the 10 Mrad dose is actually higher than that without irradiation, implying an increase in the crystallinity. Such an increase in crystallinity with irradiation had been observed earlier and is probably caused by chain scission in the copolymer allowing for an increase in the chain mobility and hence, the crystallinity.¹⁷ At higher doses, the crosslinking becomes dominant with a reduction in crystallinity.¹³⁻¹⁵

The peak associated with the original F-P transition of the unirradiated sample changes with dose quite remarkably, which is in sharp contrast with the behavior of the melt transition. For samples irradiated with doses above 50 Mrads, the F-P transition peak almost disappears, and the temperature of the very weak F-P transition changes only to a minor extent with dose (Fig. 4(b) and 4(c)). In addition, the peak temperature from DSC data ($\sim 45^\circ\text{C}$) for the copolymers irradiated in this dose range is higher than the temperature of the broad dielectric maximum ($\sim 20^\circ\text{C}$), suggesting that the two are associated with different phenomena. It is likely that the weak DSC peak observed here originates from the small residual polar regions in the copolymer, while the dielectric maximum results from the collective dipole responses and thus involves relatively long range dipolar motions.

(2.2.3.2) Structure changes on the micro- and meso-scales

The evolution of crystal with dose as revealed by room temperature X-ray data

X-ray data were obtained for copolymers irradiated with different doses including diffraction peaks perpendicular and parallel to the polymer chains, to follow structural changes in both directions. The data from the (110, 200) diffraction peak, which are due to changes in polymer inter-chain spacing and ordering perpendicular to the chains in the crystalline regions, are presented in Fig. 5. The corresponding data for (00 l) diffraction peak, which arise from the dimensional changes of unit cell along the polymer chain, are presented in Fig. 6. Both data sets were acquired at room temperature.

The crystalline phase of P(VDF-TrFE) copolymers has an orthorhombic unit cell in which the c -axis is parallel to the polymer chain.¹⁸ Because the ratio of the lattice constants of the unit cell along the " a " and " b " axes (perpendicular to the chains) is close to $\sqrt{3}$, the lattice has a quasi-hexagonal structure, resulting in the overlap of the (110) and (200) reflections.

We first discuss the X-ray data from the (00 l) reflection. Clearly, there are two peaks at $2\theta=28.29^\circ$ and $2\theta=31.53^\circ$ respectively. The peak at $2\theta=28.29^\circ$ (corresponding to a lattice space of 0.2537 nm) originates from the (001) reflection in ferroelectric (F) phase, while the peak at $2\theta=31.53^\circ$ (corresponding to a lattice space of 0.4564 nm) originates from the (002) reflection in the non-polar (NP) phase, i. e., the paraelectric α -phase or δ -phase.^{18,29} The data from the (00 l) reflection (Fig. 6) demonstrate quite clearly that the polymorphic transformation caused by irradiation is a first order process between the F and NP phases. That is, the intensity of the (001) peak in the F phase decreases

while the intensity of the (002) peak in NP phase increases with dose. There are two features that should be noted here: (i) Although there is a large variation in the peak intensity for the F and NP phases as the dose changes, the peak position remains nearly the same for all the doses. (ii) The evolution of the F-phase peak with dose also displays a re-entrant behavior. Initially, as the dose increases, the peak intensity decreases until a dose of 75 Mrads is reached, at which point, the sample shows very little sign of the presence of a F-phase peak. Beyond 75 Mrads, there is a gradual increase in the peak intensity for the F-phase. This re-entrant behavior is consistent with observations from polarization loops and dielectric data for the same doses.

By employing the Scherrer equation, the size of the coherent X-ray reflection region D_{hkl} can be estimated,¹⁹

$$D_{hkl} = \frac{0.9\lambda}{B \cos(\theta)}$$

where λ is the X-ray wavelength, B is the full width at half maximum (FWHM) of the reflection peak (hkl) and θ is the peak position. In the F phase, the coherent X-ray reflection region is determined by the polarization domain size; in the NP phase, it corresponds to the crystallite size. In Fig. 7(a), we plot D_{001} for the F phase and NP phase measured for samples treated with different doses. Before irradiation, the polar domain size of the F-phase along the c -axis is about 15 nm. This value decreases with dose, due to the defects introduced by the irradiation, which break up the polarization coherence. In samples irradiated with a dose of 35 Mrad, D_{001} for the F phase is reduced to 10 nm; for samples treated with doses beyond that, the peak intensity of the F-phase drops precipitously. The NP-phase peak is visible even in samples irradiated with very low doses, a result that can be attributed to the domain boundary region and can account for its broad appearance. In samples treated with doses higher than 50 Mrads, the NP-phase peak dominates; the coherent crystallite size along the polymer chain for this phase is about 5 nm, which is much smaller than that in the F-phase.

In contrast, the X-ray data from the (110, 200) reflection, which results from changes of the lattice parameters with doses perpendicular to the polymer chains, show a markedly different evolution behavior. First, the data do not display a clearly defined two peak pattern. Furthermore, the X-ray peak position changes continuously with the irradiation dose. For instance, from 0 to 35 Mrads, the peak at the original F-phase moves to a lower angle, indicating a continuous expansion in the inter-chain dimension as shown in Fig. 7(b). Concomitantly, there is a reduction of the ferroelectric domain size from 15 nm to 7.5 nm. The expansion in the inter-chain dimension and the reduction of the ferroelectric domain size with the dose in this range indicate that the surface of ferroelectric domain changes to a NP phase. At 35 Mrads, the existence of the NP phase can be observed in the X-ray data as shown in Fig. 5 and 7(b). As the dose increases from 35 Mrads to 50 Mrads, the peak position moves to that of the NP-phase, indicating that the crystal now is predominantly non-polar. Consistent with this shift in the peak position, the (110, 200) peak width also shows a large reduction, because of the disappearance of the ferroelectric domains. In any case, at 50 Mrad, there are still some ferroelectric domains with very small sizes as shown in Fig. 7(b). For doses beyond 50 Mrads, there is only a negligible variation in the peak position. Meanwhile, in the same dose range, the peak width of the (110, 200) reflection decreases continuously until near 75 Mrads, where $D_{110,200}$ reaches 70 nm, which is close to the crystallite size measured in

the paraelectric phase, as will be shown in the next section. Increasing the dose to 100 Mrads causes a further reduction of $D_{110,200}$ to about 26 nm, caused by the reduction of the crystallite size due to increased crosslinking density.

The results show unequivocally that, the ferroelectric domain size in unirradiated samples is nearly isotropic (~ 15 nm). In P(VDF-TrFE) copolymers, the lattice symmetry dictates the polarization direction between neighboring domains in angles of 60° , 120° , and 180° .²⁰ For a ferroelectric material in equilibrium, the domain size is determined by the domain wall energy, coupling between domain walls, and crystallite size.^{21,22} In the polymers investigated here, because of the high nucleation barriers and the high defect concentrations, we believe that the domain size is controlled mainly by defects in the crystallites and the crystallite-amorphous boundary conditions, which can also be regarded as defects. Therefore, with increased doses, the concentration of defects (such as chain ends and pendant groups generated by chain scission) in the crystallites also increases, resulting in the observed reduction of the polarization domain size. Eventually, as the domain size is reduced to a value below a certain critical size, the macroscopic polarization state becomes unstable with respect to the non-polar phase, leading to the disappearance of the macroscopic polarization. From the data here, it is not clear that the domain size, whether along or perpendicular to the polymer chain, or both, determines this critical size. From the strong intra-chain coupling as well as the recent experimental results on the presence of a two-dimensional ferroelectric state in P(VDF-TrFE) films of a few molecular layers thick,²³ it seems reasonable to assume that the polar domain size along the polymer chain may play a more important role.

The temperature dependence of X-ray data for copolymers with different doses

Presented in Fig. 8 are typical X-ray data taken from the (110, 200) reflections as a function of temperature for copolymers irradiated with different doses (0, 35 Mrads, 50 Mrads, and 75 Mrads). The data from samples irradiated with 0 to 35 Mrads dose show a first-order F-P transition with temperature (two phase coexistence region). In the non-polar phase, the X-ray peak width, which becomes quite narrow, is determined by the coherent X-ray scattering region or approximately by the crystallite size along the $\langle 110,200 \rangle$ direction. It is interesting to note that the peak width of the paraelectric phase (non-polar phase) is nearly the same as that measured at room temperature in copolymers irradiated with 65 – 85 Mrads doses. This is consistent with the fact that the NP phase is dominant in polymers in that dose range. In samples irradiated at 50 Mrads or higher doses, a transition is not observed, and the lattice constant exhibits a typical thermal expansion curve of the non-polar phase.

The data also show that the crystallite size perpendicular to the polymer chain is not affected by the irradiation until above 85 Mrads (Fig. 9). On the other hand, the crystallite size parallel to the chain is reduced by the irradiation even at doses far below. Foreexample, above 75 Mrad and at room temperature, the copolymer is in the non-polar phase; therefore, the X-ray peak width should be that defined by the crystallite size. This is exemplified in Fig. 7 where D_{001} , which is the crystallite size along the $\langle 001 \rangle$ direction, is about 5 nm. This is much smaller than that of the ferroelectric domain size in the copolymer before irradiation.

Conformational changes with dose and temperature

The FT-IR spectra obtained on copolymers irradiated at different doses measured at room temperature are shown in Fig. 10(a) (Dose = 0, 35, and 75 Mrads, respectively). To quantify the conformational change with dose, we focus on three absorbance peaks at 1288 cm^{-1} for the long trans sequence ($T_{m>3}$), 614 cm^{-1} for the trans-gauche (TG), and 510 cm^{-1} for the T_3G conformations, which are due to the vibration of the CF_2 group.²⁴ Before irradiation, the spectrum is characterized by a strong absorbance peak at 1288 cm^{-1} , which diminishes with irradiation dose. In Fig. 10(b), we present a summary of the change of the three conformations with dose, extracted from the data in Fig. 10(a). In the extraction process, each absorbance peak was fitted to a Lorentzian shape. To account for possible variations in the sample thickness and therefore the absorbance, an internal standard (at 3022 cm^{-1} , which is the asymmetric stretching vibration of C-H bond) was used to calibrate those absorbance peaks of interest.²⁵ The fraction of each conformation can be calculated (data in Fig. 10(b)) following the method of Osaki *et al.*,²⁶

$$F_i = \frac{A_i}{A_I + A_{II} + A_{III}}$$

Where $i=I, II, III$, and A_I, A_{II} , and A_{III} are the absorbances of crystal forms I, II, and III, i.e., with all trans ($T_{m>4}$), T_3GT_3G' , and $TGTG'$ sequences, respectively. F_i is the fraction of chain conformation i . Prior to irradiation, the conformation of the samples is predominantly all-trans because of the ferroelectric nature of the material. The absorption bands are due to small concentrations of TG and T_3G conformations in the domain boundary regions and as well as in the inter-phase regions between the crystallite and amorphous phases, as has been observed in the X-ray data. The trends in the conformational changes with dose are very similar to those observed in the X-ray data. All three conformations exhibit slow changes with doses below 35 Mrads, but at higher doses, large changes occur. For example, at 75 Mrads, the all-trans conformation disappears and is replaced by T_3G conformations randomly mixed with TG conformations, consistent with the X-ray results that demonstrate that the crystallite is in the NP-phase.

Prior to irradiation, there is a large and relatively sharp change in the chain conformation in P(VDF-TrFE) copolymer due to the phase transition from a non-polar phase to a polar phase as the temperature is lowered through the F-P transition. However, for relaxor ferroelectrics, extensive investigations such as Raman scattering experiments carried out on inorganic materials have shown that there is a gradual increase of the population of micro-polar regions as the temperature is reduced.²⁷ In other words, there is a local symmetry breaking from the non-polar to polar ordering even though macroscopically, the sample remains non-polar.²⁸ Now the question is whether a similar explanation applies to the irradiated copolymer. To examine this question, we consider the data showing the conformational changes as the temperature is varied for the three samples under different dose treatments (Fig. 11). In the unirradiated samples, the absorbance peak intensity remains nearly constant at temperatures below 70°C . The data point at 100°C suggests a transition to the non-polar phase, as indicated by the drop of the peak intensity due to the all-trans conformation and the increase in peak intensities attributed to the T_3G and TG conformations.²⁹ In samples irradiated with a 35 Mrad dose at 100°C , the chain conformation is mainly T_3G , and there is very little indication of the all-trans conformation (the polar conformation). As the temperature is reduced, the all-

trans conformation increases nearly linearly until 30 °C. This can be compared with the dielectric data where a weakly first order transition was observed to begin at about 30 °C.

In contrast, in the sample irradiated with 75 Mrads at temperatures above 30 °C, there is no suggestion of the all-trans conformation, although a small increase of the all-trans chain conformation is seen at lower temperatures, coinciding with the Vogel-Fulcher temperature, T_f . This behavior contrasts sharply with that observed in samples not exposed to irradiation as well as samples irradiated with 35 Mrads, demonstrating that the broad dielectric peak does not correspond to a broad phase transition between a polar and non-polar phase. Furthermore, the absence of the all-trans conformation and only minor changes in chain conformations at temperatures above the broad dielectric peak are indicative of behavior that differs from that observed in relaxor ferroelectrics in inorganic relaxor ferroelectrics, in which there is a large increase in the population of local polar regions with reduced temperature, even at temperatures far above the broad dielectric constant peak.²⁸

References:

1. Charlesby, A. *Radiat. Phys. Chem.* **1991**, *37*, 5.
2. Lovinger, A. In *Radiation Effects on Polymers*, Clough, R. L.; Shalaby, S. W., Eds.; ACS Symposium Series 475, ACS, Washington, DC 1991; Chapter 6.
3. Lovinger, A. *Macromolecules* **1985**, *18*, 910.
4. Daudin, B.; Dubus, M.; Legrand, J. F. *J. Appl. Phys.* **1987**, *62*, 994.
5. Macchi, F.; Daudin, B.; Legrand, J. F. *Ferroelectrics* **1990**, *109*, 303.
6. Odajima, A.; Takase, Y.; Ishibashi, T.; Yuasa, K. *Jpn. J. Appl. Phys.* **1985**, *24*, 881.
7. Zhang, Q. M.; Bharti, V.; Zhao, X. *Science* **1998**, *280*, 2101.
8. Cheng, Z.-Y.; Bharti, V.; Xu, T.B.; Xu, H.S.; Mai, T.; Zhang, Q. M. *Sensors and Actuators A-Phys.* **2001**, *90*, 138.
9. Bharti, V.; Xu, T.-B.; Cheng, Z.-Y.; Mai, T.; Zhang, Q. M.; Ramotowski, T.; Wright, K. A. *Jpn. J. Appl. Phys.* **2001**, *40*, 672.
10. Zhang, Q. M.; Cheng, Z. -Y.; Bharti, V. *Appl. Phys. A* **2000**, *70*, 307.
11. Bharti, V.; Zhang, Q. M. *Phys. Rev. B* **2001**, *63*, 184103.
12. Zhang, Q. M.; Scheinbeim, J. *Electric Polymers*, in *Electroactive Polymer Actuators as Artificial Muscles*, Y. Bar-Cohen, Eds.; SPIE Optical Engineering Press, WA, 2001; Chapter 4.
13. Bharti, V.; Xu, H. S.; Shanthi, G.; Zhang, Q. M.; Liang, K. *J. Appl. Phys.* **2000**, *87*, 452.
14. Forsythe, J. S.; Hill, D. J. T. *Prog. Polym. Sci.* **2000**, *25*, 101.
15. Lyons, B. J. *Radiant. Phys. Chem.* **1995**, *45*, 159.
16. Tagantsev, A. K. *Phys. Rev. Lett.* **1994**, *72*, 1100.
17. Pae, K. D.; Bhateja, S. K.; Gilbert, J. R. *J. Polym. Sci. Polym. Phys.* **1987**, *25*, 717.
18. Hasegawa, R.; Takahashi, Y.; Chatani, Y.; Tadokoro, H. *Polym. J.* **1972**, *3*, 600; Toshiro, K. In *Ferroelectric Polymers*; Nalwa, H. S. Eds.; Marcel Dekker, Inc. NY 1995; Chapter 2.
19. Warren, B. E. *X-ray Diffraction*, Dover Publications, Inc., NY 1990.
20. Kepler, R. G.; Anderson, R. A. *J. Appl. Phys.* **1978**, *49*, 1232; Naegele, D.; Yoon, D. Y. *Appl. Phys. Lett.* **1978**, *33*, 132; Tashiro, K.; Kobayashi, M. *Polymer* **1986**, *27*, 667.

21. Arlt, G. *J. Mater. Sci.* **1990**, 25, 2655.
22. Lines, M. E.; Glass, A. M. *Principles and Applications of Ferroelectrics and Related Materials*, Clarendon Press, Oxford 1977.
23. Bune, A. V.; Fridkin, V. M.; Ducharms, S.; Blinov, L. M.; Palto, S. P.; Sorokin, A. V.; Yudin, S. G.; Zlatkin, A. *Nature* **1998**, 391, 874.
24. Reynolds, N. M.; Kim, K. J.; Chang, C.; Hsu, S. *Macromolecules* **1989**, 22, 1092.
25. Kobayashi, K.; Tashiro, K.; Tadokoro, H. *Macromolecules* **1975**, 8, 158.
26. Osaki, S.; Ishida, Y. *J. Polym. Sci. Polym. Phys.* **1975**, 13, 1071.
27. Burns, G.; Dacol, F. H. *Ferroelectrics* **1990**, 104, 25.
28. Cross, L. E. *Ferroelectrics* **1987**, 76, 241.
29. Tashiro, K.; Kobayashi, M. *Phase Transitions* **1989**, 18, 213.

List of Figures

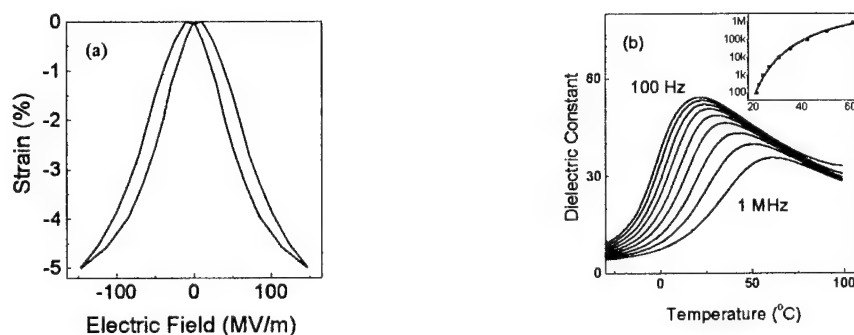


Fig.1 (a). Longitudinal strain response vs. electric field (1 Hz) observed in electron irradiated 68/32 copolymer films at room temperature. (b). Temperature dependence of the dielectric constant at frequencies of 100, 300, 1k, 3k, 10k, 30k, 100k, 300k, and 1MHz for stretched 68/32 film irradiated at 100 °C with 75 Mrad dose. Insert figure is the measured relationship (square) between the frequency and dielectric constant peak temperature and the fitting results (solid line) using Vogel-Fulcher relationship.

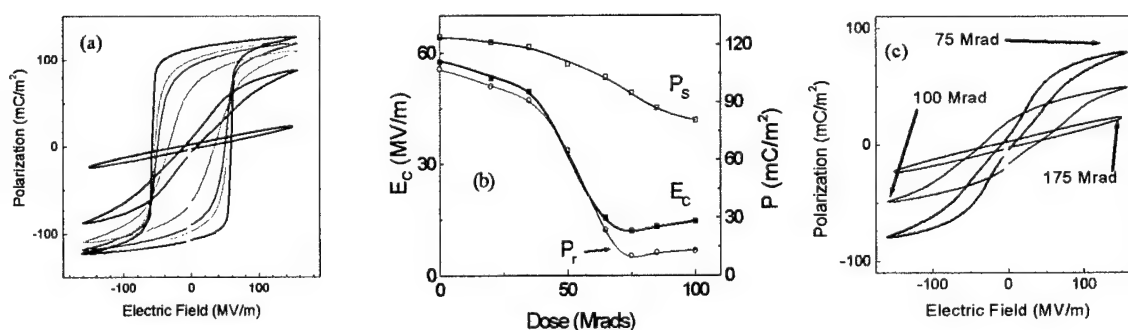


Fig.2 (a). Polarization hysteresis loops measured at room temperature and 1 Hz for copolymer films irradiated with different doses. For the polarization level from high to low, the corresponding dose is 0, 20, 35, 50, 75, and 175 Mrad respectively. (b). Spontaneous polarization P_s , permanent polarization P_r , and coercive field E_c vs. irradiation dose, where P_s , P_r , and E_c were measured at room temperature and 1 Hz using an electric field with an amplitude of 150 MV/m. (c). Polarization hysteresis loops for films irradiated with 75, 100, and 175 Mrad, respectively.

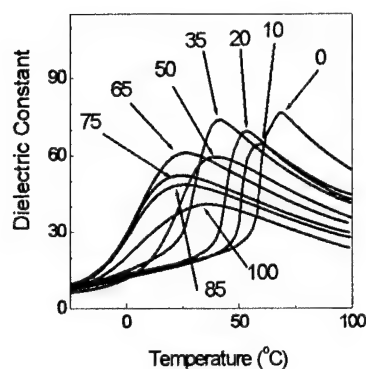


Fig.3 Temperature dependence of dielectric constant at 1 kHz measured during cooling of irradiated copolymers. The irradiation doses in Mrad are indicated in the figure.

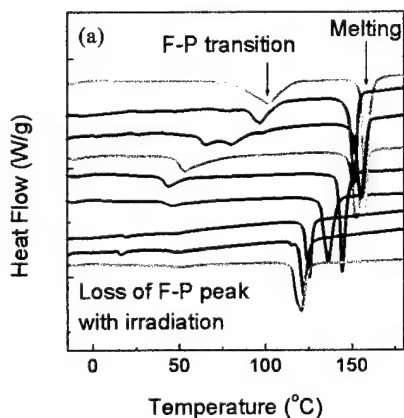


Fig. 4 (a) DSC data collected by heating irradiated copolymer from -40°C to 200°C . From top curve to bottom curve, the corresponding doses are 0, 10, 20, 35, 50, 65, 75, 85, and 100 Mrad respectively. (b). Melt temperature and F-P transition temperature. (c) Melting enthalpy and phase transition enthalpy for copolymer irradiated with different doses.

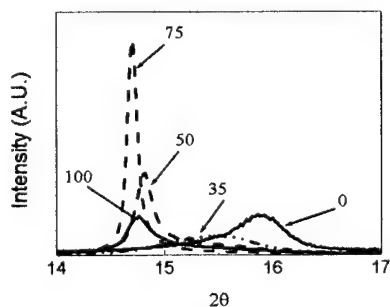
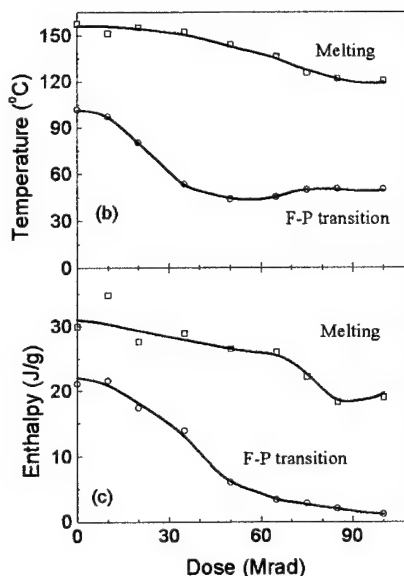


Fig.5 The (200, 110) diffraction peak observed at room temperature using the reflection scan for copolymer films irradiated with different dose. The number in the figure expresses the dose in Mrad.

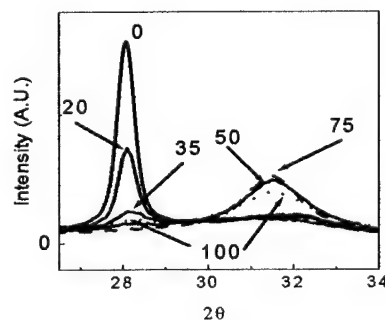


Fig.6 The (001) diffraction peak observed at room temperature using the transmission scan for copolymer films irradiated with 0, 20, 35, 75, and 100 Mrad respectively.

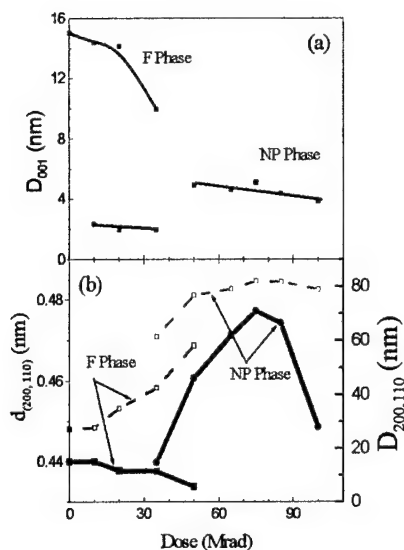


Fig. 7 (a) The irradiation dose dependence of crystallite size D_{001} parallel to the molecular chain at room temperature. (b) The dose dependence of crystalline size $D_{200,110}$ (solid line) and inter-chain spacing $d_{(200,110)}$ (dotted line) measured at room temperature. The data indicate a lattice expansion perpendicular to the chain and contraction along the chain, respectively, in the dose range from 0 to 50 Mrads.

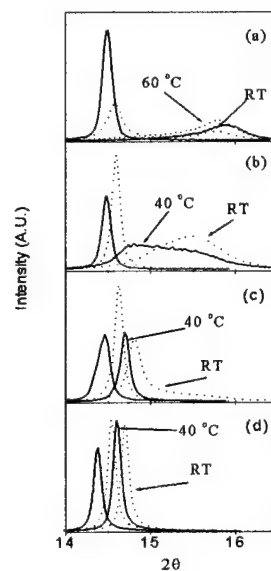


Fig. 8 The (200,110) diffraction peak observed at different temperatures using the reflection scan for unirradiated film (a) (solid line—110 °C, dotted line—90 °C, 60 °C and RT data are indicated), and irradiated films with different doses (solid line—90 °C, dotted line—60 °C, RT and 40 °C data are indicated in the figure): (b) 35 Mrad dose, (c) 50 Mrad dose, and (d) 75 Mrad dose. "RT" is room temperature.

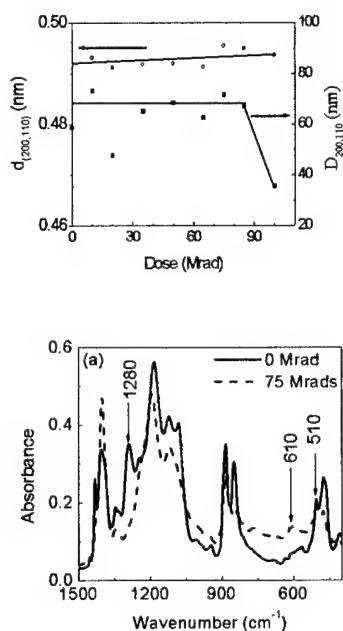


Fig. 9 The dose dependence of crystalline size $D_{200,110}$ and inter-chain spacing $d_{(200,110)}$ measured at high temperature (non-polar phase).

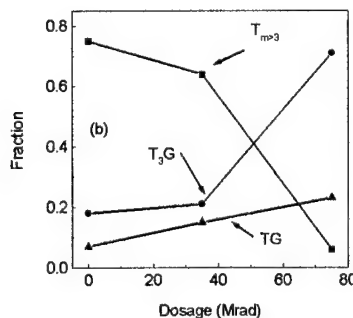


Fig. 10 FTIR data of P(VDF-TrFE) 68/32 copolymer film at room temperature. (a) The spectrum for stretched film before irradiation and stretched film irradiated at 100 °C with 75 Mrad using 1.2MeV electrons. (b) Fraction of different conformations in film vs. irradiation dose.

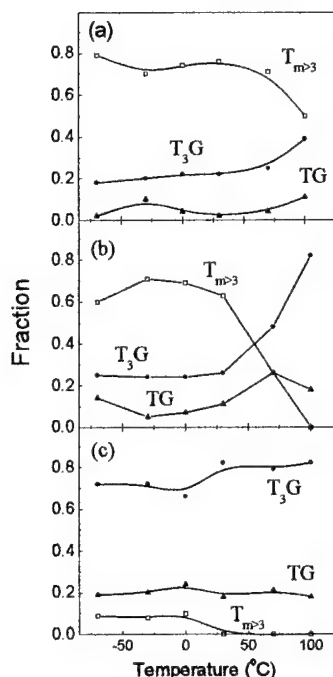


Fig. 11 Temperature dependence of fractions of different conformations in stretched 68/32 copolymer films, (a) unirradiated, (b) irradiated with 35 Mrad dose, (c) irradiated with 75 Mrad dose.

(2.2) Structure-property relationship in P(VDF-TrFE) based terpolymers

After the discovery of the high electromechanical response in high energy electron irradiated P(VDF-TrFE) copolymers, in 1997, we proposed to carry out study in PVDF based terpolymer systems. Under the funding of a DARPA program, a series of terpolymers have been synthesized and their electromechanical responses have been characterized. Although in P(VDF-TrFE) copolymers, addition of HFP, CTFE, CFE, etc. can convert the polymer into a ferroelectric relaxor, the level of the field induced strain of those terpolymers is vastly different. The reason behind it is that although the randomness introduced by the bulkier ter-monomer can destroy the normal ferroelectricity, the field induced strain is due to the local conformation change between the TG and all trans conformations. Therefore, the question is what is the best ter-monomer to be incorporated into the copolymer. The answer to this is that the ter-monomer should favor both intra-chain and inter-chain TG conformation. From the steric and electrostatic consideration, it seems that among the possible monomers, CFE ($-\text{CH}_2\text{-CFCl}-$) is probably the best choice which is also confirmed by the molecular simulation.

X-ray and FT-IR were used to characterize the micro-structure changes due to the addition of the termonomer CTFE ($-\text{CF}_2\text{-CFCl}-$) and CFE. Apparently, CTFE will favor the intra-chain trans conformation because of the large size of F ion and the charge repulsion between the F_2 and FCl .

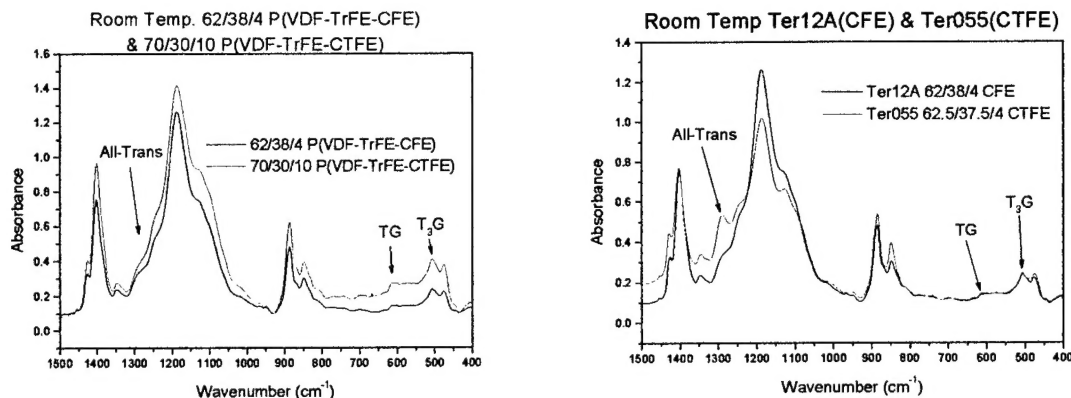
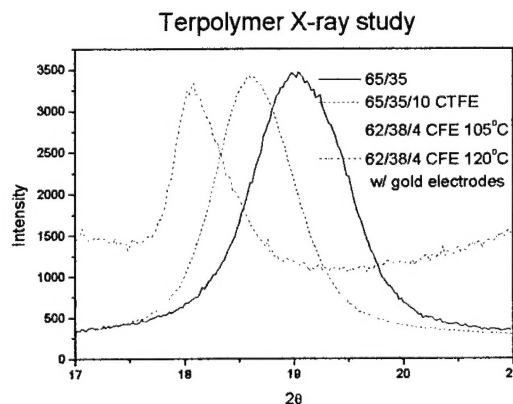


Fig. 12 (left) the comparison of the FT-IR spectra of VDF-TrFE-CTFE 70/30/10 and VDF-TrFE-CFE 62/28/4 (left). Apparently, only 4 mol% CFE can effectively eliminate the all trans conformation in the copolymers compared with 10 mol% CTFE needed. Fig. 12 (right) is the comparison of the spectra of VDF-TrFE-CTFE 62.5/37.5/4 and VDF-TrFE-CFE 62/38/4. Clearly, in the terpolymer with 4 mol% CTFE, there are still substantial amount of all trans conformations compared with the terpolymer with 4 mol% CFE.

Fig. 13 is the comparison of the X-ray data which again show the effectiveness of CFE in reducing the all trans conformation (smaller inter-chain lattice spacing):

The smaller amount of CFE in the terpolymers also implies that the terpolymer possesses high crystallinity and hence high elastic modulus. Indeed, the terpolymer P(VDF-TrFE-CFE) 62/38/4 mol% exhibits a strain of more than -5% with the elastic modulus higher than 1 GPa, which result in a very high elastic energy density ($>1 \text{ J/cm}^3$) and an electromechanical coupling factor ~ 0.5 , the highest in the electroactive polymers. In comparison, the best terpolymer of P(VDF-TrFE-CTFE) exhibits a field induced strain of -4% with an elastic modulus at 0.4 GPa, which has an elastic energy density $\sim 0.32 \text{ J/cm}^3$, much lower than the terpolymer of P(VDF-TrFE-CFE).



(2.3) High dielectric constant polymers based on grafted CuPc

Our earlier effort has shown that in the composites of P(VDF-TrFE) matrix and CuPc filler, a high dielectric constant ($>1,000$) can be obtained. The problem with the direct physical mixing of the two is that the sample is not very uniform which results in a low breakdown field ($\sim 1 \text{ MV/m}$). However, even with such a high field, an electrostrictive strain of 0.3% has been achieved. In this time period, one of the significant results is that we have succeeded in grafting CuPc to the P(VDF-TrFE) main chain and as a result, the “composite” shows a very high dielectric constant (at 10 Hz, it is more than 7,000, see Fig. 14). Because of the tight funding, the post-doc, H. Xu had left the group and now

this effort has been stopped. We are in the process of working with groups in other countries to continue this effort.

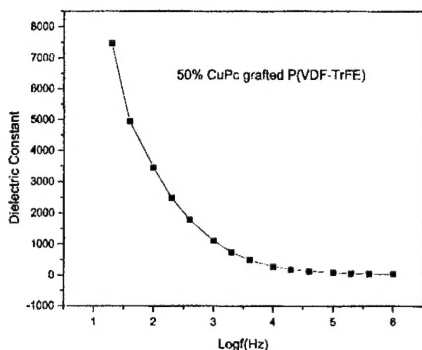


Fig. 14 Dielectric constant of CuPc grafted polymer.

III. Publications and Presentations:

(3.1) Publications:

Ferroelectric and electromechanical properties of poly(vinylidene-trifluoroethylene-chlorotrifluoroethylene) terpolymer, *Applied Physics Letters*, **78**, 2360 (2001).

High dielectric constant composites based on metallophthalocyanine oligomer and poly(vinylidene-trifluoroethylene) copolymer. *Journal of Applied Polymer Science*, **82**, 70 (2001).

Structural Changes and Transitional Behavior Studied From Both Micro and Macro Scales in the High-Energy Electron-Irradiated Poly(vinylidene fluoride-trifluoroethylene) Copolymer. *Macromolecules* (2001).

Electro Polymers, Q. M. Zhang and J. Scheinbeim, Chapter 4 in "Electroactive Polymer Actuators as Artificial Muscles" ed. Y. Bar-Cohen, SPIE Optical Engineering Press, WA 2001

PVDF and Its Copolymers with TrFE, Q. M. Zhang, V. Bharti, and G. Kavarnos, in "The Encyclopedia of Smart Materials" John Wiley&Sons, Inc. 2001

(3.2) Presentations:

Q. M. Zhang, V. Bharti, Z. Y. Cheng, H. S. Xu, T. B. Xu, T. Ramatowski, L. Ewart, and R. Ting. Electrostrictive and Relaxor Ferroelectric Behavior of P(VDF-TrFE) Based Polymers – A Review. 12th IEEE International Symp. Appl. Ferro. (Hawaii, Sept. 30-Aug. 3, 2000). (Invited)

V. Bharti, Z. Y. Cheng, and Q. M. Zhang. Dielectric Relaxation and Weak Polarization Response in Relaxor Ferroelectric P(VDF-TrFE) Copolymer. 12th IEEE International Symp. Appl. Ferro. (Hawaii, Aug. 2000).

Z.Y. Cheng, T. B. Xu, V. Bharti, S. Gross, T. Mai, Q. M. Zhang, T. Ramotowski, L. Ewart, and R. Ting. Electrostrictive Effect and Load Capability in Electron Irradiated P(VDF-TrFE) Copolymer. IEEE 12th International Symp. Appl. Ferro. (Hawaii, Aug. 2000).

Q. M. Zhang. Electrostriction and Relaxor Ferroelectric Behavior in Electron Irradiated Polymers. 4th Internat. Symp. Ionizing Radia. & Polym. (Gouvieux-Chantilly, France, Sept. 25-27, 2000). (Invited)

Q. M. Zhang and Z.Y. Cheng. Recent Advances in Electromechanical and Electronic Properties of P(VDF-TrFE) Based Ferroelectric Polymers. The Knowledge Foundation's International Conference on Novel Materials for Electronics Miniaturization (San Francisco, CA, Nov. 2-3, 2000). (Invited)

Q. M. Zhang, H. S. Xu, Z. Y. Cheng, M. Tian, R. Ting. Electrostrictive P(VDF-TrFE)-based Terpolymers and Its Device Performance. SPIE 8th Annual International Symposium on Smart Structures and Materials (Newport Beach, CA, March 4-8, 2001).

Q. M. Zhang, Electroactive polymers for large sensor and actuator arrays. DARPA DSRC Workshop on Electrotexile, March 7, 2001, Washington DC. (Invited)

Q. M. Zhang. Recent Development of P(VDF-TrFE) Based High Strain Polymers. Workshop on Cephalopod Arms, Tentacles and Senses as Inspiration for Novel Robotic Manipulators. Marine Biological Laboratory, National Academy of Science Jonsson Conference Center, Woods Hole, MA (May 3-6, 2001) (Invited)

H. S. Xu, D. Olson, Z.-Y. Cheng, T. Ramotowski, G. Kavarnos, and Q. M. Zhang. Micro-structure-properties of P(VDF-TrFE) Based Polymers. 2001 US Navy Workshop on Acoustic Transduction Materials and Devices. May 14-16, 2001, Baltimore, MD.

Q. M. Zhang. Recent Development of P(VDF-TrFE) Based High Strain Polymers. 2001 US Navy Workshop on Acoustic Transduction Materials and Devices. May 14-16, 2001, Baltimore, MD.

Z. Y. Cheng, H. Xu, T. B. Xu, W. Chen, R. Meyer, J. Hughes, and Q. M. Zhang. Device Performance of Electrostrictive P(VDF-TrFE) Based Actuators and Transducers. 2001 US Navy Workshop on Acoustic Transduction Materials and Devices. May 14-16, 2001, Baltimore, MD.

Q. M. Zhang. High Electromechanical Responses and Microstructures of Modified P(VDF-TrFE) Based Polymers. Princeton University, NJ, May 29, 2001.

Q. M. Zhang. Electrostrictive Polymers--A Defectes Structure Modified Polymers.
UCLA, January 12, 2001

IV. Technology Transfer:

Two related activities:

A start-up company has been formed: Electro Polymer Technology, Inc. which is in the process of commercializing the high performance electroactive polymers

Medtronic, a medical company, is interested in using the polymers developed for their drug delivery systems and charge storage devices

V. Patent:

Q. M. Zhang, H. S. Xu, and Z. Y. Cheng. "P(VDF-TrFE) Based Terpolymers for Electromechanical and Dielectric Applications" Provisional patent filed (No. 60/280,303).

Q. M. Zhang, H. S. Xu, and Z. Y. Cheng. "High Dielectric Constant Polymer Systems Based on Metallophthalocyanine-Polymer Composites" Provisional patent filed (No. 60/283,755).